Synthesis and characterization of novel starburst phase transfer catalyst

Siji Mathew, Divia N, T D Radhakrishnan Nair & Karickal R Haridas*

School of Chemical Sciences, Kannur University, Payyanur Campus, Edat P.O. 670327, India

E-mail: krharidas2001@yahoo.com

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A new phase transfer catalyst, 3,5-bis[(2-methyl-naphthylene-1-yl)-phenylamino-phenyl]-butyl-(2methoxy-naphthalene-1-yl)-phenylammonium bromide (BPBPB) has been synthesized, characterized using spectral analysis and its catalytic activity ascertained. Efficiency of BPBPB is studied using etherification of phenol and compared with tetra butyl ammonium bromide [TBAB].

O-Alkylation of naphthol, N-alkylation of indole and halogen substitution reactions are carried out using BPBPB and its efficiency is compared with reported PTCs. BPBPB gives high yield of product, the time for completion of the reaction is short and is required in a very low concentration. Almost 95% of this catalyst is regenerated and reused.

Keywords: Starburst phase transfer catalyst, optimization, alkylation, regenerative catalyst

Phase transfer catalysis (PTC) is a versatile, well-established green chemistry synthetic technique which can be applied with several advantages and with economic viability to a number of organic liquid biphas reactions1. PTC has been quite successful in C-, N-, O- and S-alkylations involving S\textsubscript{N}2 type reactions. These reactions also proceed with selectivity to give rise to high yields of the product2. Basic work in our laboratory is to synthesize hole transporting materials for the fabrication of optoelectronic devices3,4. In continuation of this work a starburst tertiary amine compound which showed the properties like high organophilicity, large lipophilicity and high electron capturing capacity is synthesized. As this starburst compound showed the above properties, we thought it could be quaternarised and then which may act as a good PTC.

The present investigation is focused on the synthesis of 3,5-bis[(2-methyl-naphthylene-1-yl)-phenylamino-phenyl]-butyl-(2-methoxy-naphthalene-1-yl)-phenylammonium bromide [BPBPB] to be used as a PTC. This is a quaternary ammonium compound with starburst substituents. It is successfully used in the etherification of phenol and naphthol, N-Alkylation of indole and halogen substitution reactions. Catalytic efficiency of the synthesized starburst PTC is compared with tetra butyl ammonium bromide [TBAB].

Optimization of concentration

The yields of butyl phenyl ether at various concentrations of TBAB and starburst PTC in similar reaction conditions are given in Table I. It is clear that even at very low concentration the yield of the conversion is higher (95.2%) when BPBPB is used as PTC. At all concentrations BPBPB gives higher yield compared with TBAB. The increased reactivity of BPBPB is due to the increase in the total number of carbon atoms in the aryl group of the cation. The reactive site of TBAB contains a symmetric cation which is favourable for the attack of the nucleophilic

![Scheme I](image-url) — Substitution reaction between sodium phenolate and n-butyl bromide.
reagent. Even though, BPBPB contains an unsymmetrical cation, its reactivity is higher. This is because of the high organophilicity and large steric hindrance, which overcomes the unsymmetrical effects.

A pictorial representation of the effect of these catalysts on the variation of concentration of PTCs used and respective yields of the products are shown in Figure 1.

**Optimization of time**

The relation of time and optical density (OD) for the completion of the butyl phenyl ether forming reaction using all three PTCs under similar reaction conditions are given in Table II. Optical density is measured at 294 nm which corresponds to the absorbance maxima of butyl phenyl ether. At all intervals of time optical density measured for the product obtained by using BPBPB as catalyst is higher compared with that of the product obtained using TBAB. BPBPB gives maximum optical density of 1.3360 at 3 hr while TBAB gives maximum optical density of 1.0556 at 4 hr, Table II also indicates that the reaction using BPBPB gets completed faster with high yield when compared with TBAB under similar conditions of reaction. The reason for this may be because of the enhanced activity of the starburst catalyst due to large surface area and more reactive sites. The optical densities of butyl phenyl ether at various time intervals using all three PTCs are shown in Figure 2.

In order to test the efficiency of BPBPB, we carried out a representative reaction (etherification reaction, formation of butyl phenyl ethers) without using PTC under the similar conditions of reaction using TBAB. BPBPB gives maximum optical density of 1.3360 at 3 hr while TBAB gives maximum optical density of 1.0556 at 4 hr, Table II also indicates that the reaction using BPBPB gets completed faster with high yield when compared with TBAB under similar conditions of reaction. The reason for this may be because of the enhanced activity of the starburst catalyst due to large surface area and more reactive sites. The optical densities of butyl phenyl ether at various time intervals using all three PTCs are shown in Figure 2.

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**Table I** — Yield of butyl phenyl ether at various concentrations of TBAB and Starburst PTC

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>TBAB</th>
<th>Starburst PTC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. (mol×10⁻⁴)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.05</td>
<td>60.2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>69.7</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>72.9</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>75.8</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>85.4</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>90.1</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>88.6</td>
</tr>
</tbody>
</table>

Sodium phenoxide: 0.03 mole; butyl bromide: 0.03 mole; toluene: 25 cm³; temperature: 70°C; time: 4 hr.

**Table II** — Optical density of butyl phenyl ether at various time intervals using PTCs

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Time (hr)</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BPBPB</td>
<td>TBAB</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.1120</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.5365</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>0.6773</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.9309</td>
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<td>1.2368</td>
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<td>1.1571</td>
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<tr>
<td>9</td>
<td>4.5</td>
<td>1.1281</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>1.0718</td>
</tr>
</tbody>
</table>

Sodium phenoxide: 0.03 mole; butyl bromide: 0.03 mole; toluene 25 cm³; temperature: 70°C; BPBPB: 0.0001 mole, TBAB: 0.003 mole.

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![Figure 1](image1.png)  
**Figure 1** — Variation of concentration of PTCs with yield

![Figure 2](image2.png)  
**Figure 2** — Optical density of butyl phenyl ether at various time intervals using PTCs
reactions with other reported PTCs. We have also compared the above reactions using BPBPB are listed in Table III, (Scheme II). We have also compared the above reactions with and without PTC. Another highlight of the work is the use of minimum amount of solvents (15 mL against 250 mL) for the reaction without affecting the yield. This will indicate the importance of the work as a green chemistry synthesis.

Using BPBPB, we have carried out O-alkylation of naphthol, N-alkylation of indole and halogen substitution reactions. The results of phase catalyzed reactions using BPBPB are listed in Table IV, (Scheme II). We have also compared the above reactions with other reported PTCs.\(^5,9-12\)

**Regenerative catalyst**

BPBPB is regenerative to about 95% in weight. In order to test the recycling and reusing capability of BPBPB, after the first reaction, whole of the catalyst is separated by extraction, washed, dried and purified by column chromatography. It is then reused under the same conditions. We have observed that at least 95% by weight of the catalyst is reusable (100% regenerative).

**Experimental Section**

The reagents: TBAB (SRL India), 2-naphthol, aniline, mohr’s salt (Merck, India), 1-bromoethane, 1-bromobutane, 2-bromobutane, indole, (Loba Chemie) were purified as per common laboratory procedure before use. Silica Gel (60-120 mesh, SRL) and Bromine (Merck) were used as such. The solvents were distilled before use according to procedures available in literature. Spectroscopic grade solvents (Merck) were used for UV-visible spectrometric analysis.

Melting points were determined in open capillaries using melting point apparatus (JSGW, Gujarat). Infrared (IR) spectra were measured on a Shimadzu FTIR 8400 S spectrometer as potassium bromide (KBr) disc. Ultraviolet-visible (UV-vis) spectra were recorded as a diluted solution in spectroscopic grade ethanol on a UV-vis. Shimadzu 1700 using 1.0 cm length quartz tube. \(^1\)H and \(^13\)C NMR spectra were recorded on a NMR-JEOL GSX-400 spectrometer with tetra methylsilane as the internal reference using CDCl\(_3\) as solvent in all cases.

The yields of the products are calculated on the basis of the number of moles of reactants used and that of the pure products obtained.

**Catalyst Preparation**

**Methoxy naphthylamine, 1**

Conc. H\(_2\)SO\(_4\) (5 mL) and 2-methoxy naphthalene (1.58 g, 0.01 mole) were taken in a round bottom flask equipped with a condenser. It is cooled and temperature is maintained so that it does not exceed 5° C. To this 4 mL of conc. HNO\(_3\) was added dropwise with stirring. The solution was stirred for one hr at 0° C, one hr at RT and one hr at 60° C. The contents of the flask were cooled and poured into ice, neutralized with 40% NaOH. The yellow compound obtained is filtrated, 1.64 g of this product (0.008 mole), 1.5 g of mohr’s salt, ethanol (20 mL), water (5 mL) and conc. HCl (0.5 mL) were heated in a round bottom flask on a stem bath for one hr. The product was extracted from the mixture by washing with hot ethanol and dried. The yellow solid thus obtained was recrystallized from ethanol.

Yield: 75.1%; m.p. 72° C; UV-vis. (ethanol): 385, 354, 323 nm; IR (KBr): 3467, 3379 (-NH\(_2\)); 3029 (Ar-H), 2842, 1434 (-OCH\(_3\)), 1250 cm\(^{-1}\) (C-N); \(^1\)H NMR (CDCl\(_3\)): δ 3.9 (3H, -OCH\(_3\)), 4.0 (2H, -NH\(_2\)), 7.31-7.44 (6H, Ar); \(^13\)C NMR (CDCl\(_3\)): δ 56 (OCH\(_3\)), 119.1, 119.8, 119.5, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2 (1-10 C).
The organic phase was separated, washed with water (100 mL × 2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with ethanol gave yellow solids.

Yield: 40.5%; m.p. 50°C; UV-vis. (ethanol): 308, 458, 341 nm; IR (KBr): 3429 (N-H), 3071, 2950 (Ar-H), 2843, 1435 (-OCH\textsubscript{3}), 1218 (C-O-C), 1250 cm\textsuperscript{-1} (C-N); \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta \) 3.9 (9H, -OCH\textsubscript{3}), 4.0 (3H, NH), 7.1-8.7 (21H, Ar); \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \( \delta \) 56 (OCH\textsubscript{3}), 96.8 (11, 13, 15 C), 145 (12, 14, 16 C), 119.1, 119.5, 119.8, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2 (2-10 C).

Scheme II — Synthetic route for the synthesis of BPBPB.

The compound 3a, 4.2 g (0.0071 mole), 2.2 mL of bromobenzene (0.0213 mole), 200 mg of CuCl and 1.0 g of K\textsubscript{2}CO\textsubscript{3} (dried at 110°C) were refluxed together with 20 mL dichlorobenzene 10 hr at 60°C. After removal of the solvent \textit{in vacuo}, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hr. Ethyl acetate (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water (100 mL × 2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with hexane gave yellow needles.

Yield: 40.1%; m.p. 47°C UV-vis. (ethanol): 358, 364, 286 nm; IR (KBr): 3084, 2981 (Ar-H), 2842, 1435 (-OCH\textsubscript{3}), 1219 (C-O-C), 1259 cm\textsuperscript{-1} (C-N); \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta \) 3.97 (-OCH\textsubscript{3}), 7.19-8.7 (36H, Ar); \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \( \delta \) 56 (OCH\textsubscript{3}), 96.8 (11, 13, 15 C), 145 (12, 14, 16 C), 119.1, 119.5, 119.8, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 138.1, 141.6. (2-10 C, 17-22 C).

\textbf{N,N,N'}-Tris-(2-methoxy-naphthalen-1-yl)-N,N,N'-triphenylbenzene-1,3,5-triamine, 3

The compound 3a, 4.2 g (0.0071 mole), 2.2 mL of bromobenzene (0.0213 mole), 200 mg of CuCl and 1.0
Synthesis of 3, 5-bis [2-methyl-naphthylene-1-yl]-phenylamino-phenyl]-butyl-(2methoxynaphthalene-1-yl)-phenylammonium bromide (BPBPB), 4

N,N,N’-Tris-(2-methoxy-naphthalen-1-yl)-N,N,N’-triphenylbenzene-1,3,5-triamine, 11.47 g (0.014 mole) in dry ethanol (25 mL) was mixed with 2.17 mL of 1-bromobutane (0.02 mole). The contents were heated for 28 hr at 70°C with constant stirring. After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hr. Diethyl ether (150 mL) and water (100 mL were added. The organic phase was separated, washed with water (100 mL × 2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with ethanol gave yellow solid.

Yield: 45.1%; UV-vis (ethanol) 358, 364, 391 nm; IR (KBr): 3343 (NH$_2$), 3074, 2940 (Ar-H), 2843, 1435 (-OCH$_3$), 1218 (C-O-C), 1259 cm$^{-1}$ (C-N); $^1$H NMR (CDCl$_3$): δ 0.96-3.33 (9H, butyl), 3.95 (9H, -OCH$_3$), 7.01-8.2 (36H, Ar); $^{13}$C NMR (CDCl$_3$): δ 13.7, 21.6, 25, 68.3(C$_6$H$_5$), 56(OCH$_3$), 106, 114, 116, 119, 119.1, 119.5, 119.8, 120.2, 121.5, 122.9, 123.4, 124, 124.4, 125.1,126,127, 128, 129, 129.4, 130, 135,141.2, 141.6, 142, 158 (aromatic C atom).

The tertiary ammonium compound contains three similar nitrogen atoms. After quaternarisation only one nitrogen gets quaternarised. The NMR data clears this point. As all three nitrogens are similar, the attachement of butyl group to the nitrogen is immaterial.

Conclusion

PTC methodology is an important addition in the arsenal of the organic chemist as a green chemistry synthetic tool. The use of BPBPB as a catalyst in the PTC technique offers convenient conditions for a wide variety of reactions to be carried out with ease. The starburst PTC used reactions helps to increase yield. Moreover, it is also possible to recover 95% of this very useful catalyst material. The optimization data indicates that BPBPB is required only in a very minute concentration (30 times lesser) when compared with TBAB. Reaction time also is considerably less when compared with other PTCs. Due to the high molecular weight organic structure of the starburst catalyst, its organophilicility is high and hence the lipophilicity of the catalyst cation is also high. This together with the presence of large surface area, steric hindrance and large number of reactive sites helps it to function as a better PTC. One more point which adds to its reactivity is cavity like structure of starburst PTC which may also enhance the reactivity rate and give high yield. Theoretical studies are going on to evaluate its cavity structure. Further studies are in progress for the synthesis of various other Starburst PTCs which is expected to create further revolution in green chemistry organic syntheses.

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